VII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

ON THE ACTION OF PHOSPHOROUS TRICHLORIDE ON ANILINE.

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The only paper on this subject which we have been able to find was published by Tait in 1865;* in it he describes the product of the action of phosphorous trichloride on aniline as a white salve-like mass easily soluble in water, alcohol, and ether, which, when freed from an excess of aniline, had the composition $(C_6H_5NH)_3P3HCl$, gave a chlorplatinate and several double salts, but yielded no satisfactory result when he attempted to set free the base.

We were induced to take up the study of this reaction by the hope that a further investigation of Tait's substance might lead to interesting results; but in this we were disappointed, as we have not succeeded in obtaining it, and, as far as our experiments go, are inclined to think it must have been a mixture instead of a definite compound. At the same time, we cannot state with absolute certainty that it is not present in the product formed when a decided excess of aniline is used, since the impossibility of continuing our work after the beginning of the summer vacation prevented us from making the investigation of this product as thorough as we wished. For the same reason other parts of this research can be published only in a very fragmentary and imperfect condition.

The isolation of the compounds containing phosphorus formed by the action of phosphorous trichloride on aniline, in the proportion of one molecule to three, is surrounded by difficulties which we have found insurmountable; but, in spite of this, our experiments have determined with a fair degree of certainty the nature of these compounds, as will appear from the following general statement of our results, and the argument which can be based upon them.

* Jahresbericht der Chem. 1865, p. 411. Instit. 1865, p. 254.

When aniline is added to phosphorous trichloride in the proportion of three molecules of the former to one of the latter, the product, a variable mixture of aniline chloride and a substance containing phosphorus, gives a clear solution with water or alcohol. If, however, this product is heated, a waxy mass is obtained, which is soluble in alcohol; but water throws down from this solution a white precipitate having the formula $(C_6H_5NH)_2PHO$. Of the three most probable products of the reaction of phosphorous trichloride and aniline,

(1) $C_6H_5NHPCl_2$,
(2) $(C_6H_5NH)_2PCl$,
(3) $(C_6H_5NH)_3P$,

only (2) could yield $(C_6H_5NH)_2PHO$ by the action of water or alcohol, and we therefore infer that $(C_6H_5NH)_2PCl$ exists in the product after it has been heated. On the other hand, this substance cannot exist in the original product, as this dissolves in water without residue, whereas $(C_6H_5NH)_2PCl$ is converted by water into the insoluble $(C_6H_5NH)_2PHO$; but it must be formed from one of the constituents of the crude substance during the heating. Of the two probable products of the reaction, (1) and (3), mentioned above, it is hard to see how (3), $(C_6H_5NH)_3P$, by heating with aniline chloride, could be converted into $(C_6H_5NH)_2PCl$, while (1), $C_6H_5NHPCl_2$, could easily undergo this change under these conditions; from which we conclude that $C_6H_5NHPCl_2$ and aniline chloride are the products of the action of aniline on phosphorous trichloride under the conditions mentioned. This conclusion is supported by the fact that alcohol or water acts violently on the original product forming aniline phosphite, and it is highly improbable that $(C_6H_5NH)_3P$ would give such a violent reaction.

The remainder of this paper contains a detailed account of the experiments on which the above conclusions are based, a description of the properties and behavior of the new substance $(C_6H_5NH)_2PHO$, and a somewhat fragmentary account of two crystalline substances formed by boiling the crude product with an excess of aniline, one of which may be a derivative of $(C_6H_5NH)_3P$, although this point needs confirmation by further experiments.

Action of Phosphorous Trichloride on Aniline.

When aniline is added to phosphorous trichloride, the reaction is attended with so much heat, that each drop of the aniline hisses like

red-hot iron in water when it touches the trichloride; and, if the substances are mixed in about the proportion of three molecules of aniline to one of the trichloride, the product is a hard white solid, with no trace of the salve-like consistency described by Tait. It was proved to be a mixture by the following analyses of three different preparations, which were freed from an excess of either reagent by washing with ether before analysis.

	I.	II.	III.
Carbon	50.82	54.41	43.59
Hydrogen	6.28	7.07	7.10
Chlorine	19.38	23.15	
Phosphorus	5.48	2.92	

In the hope of isolating the phosphorus compound, the action of various solvents on the mass was studied, — of all the common solvents, water, alcohol, methyl alcohol, and acetone were the only ones in which it was not essentially insoluble; but, as we found that acetone dissolves aniline chloride, there was no prospect of achieving the purification of the phosphorus compound by its means, and either water or alcohol decomposed it, giving a clear solution,* which, on evaporation, left a viscous residue, apparently composed of chloride and phosphite of aniline, as it deposited crystals of the former after standing for some time, and upon solution in water and addition of plumbic acetate gave a heavy white precipitate, which, freed from plumbic chloride by washing with hot water, was proved to be plumbic phosphite, by the following analysis: —

0.6986 gr. of the salt gave 0.7380 gr. of plumbic sulphate.

	Calculated for $PbHPO_3$.	Found.
Lead	72.13	72.16

From this result it is probable that no anilidophosphorous acid was formed.

From what has been said, it appears that the product described above differs from Tait's in consistency, in its solubility in ether, and in composition; but if, instead of fulfilling the conditions given above, the trichloride is added to a large excess of aniline, a substance is obtained which resembles Tait's in its salve-like consistency and the fact that it gives a considerable extract with ether; at the same time, we cannot think that it has the composition ascribed to it by him,

* When water was used, there was sometimes a slight residue of $(C_6H_5NH)_2PHO$.

because our analyses given above show that the substance must contain aniline chloride, and this would not have been removed by mere solution in water, the only purification to which it was submitted by Tait. We may add, that the solid matter apparently extracted by ether was really dissolved in the excess of aniline, as it proved insoluble in ether after the aniline was removed, and, as aniline dissolves aniline chloride, we saw no prospect of purifying the phosphorus compound in this way. If, on the other hand, an excess of phosphorous trichloride was used, the product was a white compact mass, from which a considerable amount of solid matter was extracted with ether; but this was due evidently to its solubility in phosphorous trichloride rather than in ether, and, as it contained only two per cent of phosphorus, it was not thought worth while to pursue this part of the subject further.

Action of Heat on the Original Product.

If the mixture, analyses of which were given above, is heated, it turns orange-red, and gives off aniline chloride, the purity of which was determined by analysis, and a small quantity of a phosphorescent gas, probably phosphoretted hydrogen. This change takes place slowly and partially even at 100°, much more rapidly and completely at 150°, or at even higher temperatures. We usually heated the mass in a porcelain dish over a free flame, regulating the temperature so that aniline chloride sublimed off freely, but no spontaneously inflammable phosphoretted hydrogen was given off. The product when heated with alcohol gave a colorless solution, and a residue of an orange or red color, according to the length of time it had been heated. As this residue was insoluble in all solvents, and could not be purified completely by washing, we are in doubt as to its precise nature; but, as one preparation contained as much as 81.73 per cent of phosphorus, it cannot be an organic compound, but is either amorphous phosphorus, or the red oxide or solid hydride of that element. The alcoholic solution when treated with water gave a white precipitate of $(C_6H_5NH)_2PHO$, while aniline chloride and phosphite were left in solution with, so far as we could find, no other substances. The formation of the red body is not essential to the production of the mother-substance of $(C_6H_5NH)_2PHO$, as we obtained, by short heating in a dry test-tube, a yellowish waxy mass, which dissolved completely in alcohol and yielded a large amount of $(C_6H_5NH)_2PHO$ on addition of water; upon longer heating, however, the yellowish substance turned orange-red.

Before going to the description of the phosphorous anilid $(C_6H_5NH)_2$ PHO, we may add, that we tried to obtain the chlorine compound from which it is formed by treating the freshly heated orange mass with benzol or with absolute ether, as these solvents seemed to offer the best chance of success. The amount extracted in either case was extremely small, and possessed the most unpromising properties, the ether extract containing lumps of ordinary phosphorus imbedded in a viscous mass, while the benzol extract resembled semiliquid paint, and gave no evidence that it was a homogeneous compound; it was analyzed, however, and contained 5.12 per cent of chlorine and 21.27 per cent of phosphorus, whereas $(C_6H_5NH)_2PCl$ requires 14.17 per cent of chloride and 12.37 of phosphorus.

Phosphorous Anilid $(C_6H_5NH)_2PHO$.

The preparation of this substance has been just described. In order to purify it, as it did not crystallize, the crude precipitate was redissolved in a little alcohol, and precipitated with water; the viscous mass thus obtained was kneaded thoroughly with water, dissolved again in alcohol, and once more precipitated and washed with water; it was then dried at about 50°, and its composition determined by the following analyses of a number of different preparations: —

I. 0.3488 gr. of substance gave 0.7992 gr. of carbonic dioxide and 0.1918 gr. of water.

II. 0.2856 gr. gave 0.6502 gr. of carbonic dioxide and 0.1610 gr. of water.

III. 0.2190 gr. gave 0.5012 gr. of carbonic dioxide and 0.1180 gr. of water.*

IV. 0.3402 gr. gave after treatment, according to Carius, 0.1590 gr. of magnesic pyrophosphate.

V. 0.2016 gr. gave 0.0976 gr. of magnesic pyrophosphate.

VI. 0.4623 gr. gave 49.9 c.c. of nitrogen at a temperature of 25° and pressure of 766 m.m.

	Calculated for $(C_6H_5NH)_2PHO$.	Found. I.	II.	III.	IV.	V.	VI.
Carbon	62.07	62.47	62.04	62.41	—	—	—
Hydrogen	5.60	6.10	6.26	5 99	—	—	—
Phosphorus	13.36	—	—	—	13.05	13.52	—
Nitrogen	12.07	—	—	—	—	—	12.13

* We found it best to carry on the combustions in a closed tube, the substance being mixed with oxide of copper, as if burnt in a boat in oxygen the carbon was apt to come low, since the fused phosphoric acid prevented the complete combustion of the substance.

Properties. It forms a white amorphous mass which melts at 87°; all our attempts to obtain it in crystals have been unsuccessful; it is freely soluble in cold alcohol and in ether, insoluble in cold water, but melts under boiling water, and perhaps dissolves to a very slight extent. It is a perfectly neutral body, neither acids nor alkalies affecting it in the cold; even alcoholic sodic hydrate or sodic ethylate acts on it with difficulty; on the other hand, fuming hydrochloric acid, when boiled with it for twelve hours, decomposes it completely into aniline chloride, phosphoric acid, and a small quantity of carbonaceous substance. The formation of the aniline chloride was proved by an analysis of the sublimate, 0.2776 gr. giving 0.3114 gr. of argentic chloride,

	Calculated for $C_6H_5NH_3Cl$.	Found.
Chlorine	27.41	27.74

the formation of phosphoric acid by qualitative tests with argentic nitrate and ammonic molybdate.

Action of Nitric Acid. When the substance is gently heated with fuming nitric acid it forms a red solution, from which water precipitates a red resinous body which contains phosphorus, but was not studied further, as the quantity was not large, and its properties were uninviting. By far the principal products of the reaction were contained in the aqueous solution, which left on evaporation yellow crystals having acid properties, and easily characterized by their appearance and melting-point, 120°, as picric acid. Another preparation yielded instead of picric acid the unsymmetrical metadinitrophenol, melting at 113°–115°. These results can be explained by supposing that the nitric acid saponifies the anilid, forming aniline nitrate and phosphoric acid, and that the former is afterwards converted into the nitrophenols by the combined action of nitrous and nitric acids.

Action of Acetic Anhydride. If phosphorous anilid is heated with acetic anhydride and fused sodic acetate on the water-bath, and the product extracted with ether, a viscous mass is obtained, which gradually becomes partially converted into crystals free from phosphorus, melting at 112° after recrystallization from water, and therefore acetanilid.

From all the observations described above it appears that the substance behaves like an anilid of phosphorous acid.

Action of an Excess of Aniline on the Original Product.

If the immediate product of the action of phosphorous trichloride and aniline, or this product after it has been heated, is boiled for some time with an excess of aniline, there results a mixture of various substances from which we have succeeded in isolating the orange-red substance and phosphorous anilid already described, chloride and phosphite of aniline, and a crystalline substance melting at 208°. There seems to be also a substance with a higher melting-point, and on one occasion a body melting at 150° was obtained; unfortunately we were obliged to break off work on this part of the subject before we had done more than analyze the two substances melting at 208° and 150° respectively, so that we have as yet no satisfactory data for determining their constitution, and also have been able to make no exhaustive search for other products.

Substance melting at 208°. This compound is obtained from the mixed products of the reaction by washing out the soluble salts with water, extracting the residue with hot alcohol, and purifying the extract by crystallization from alcohol, till it shows a constant melting-point. It was dried at 100° and analyzed.

I. 0.3352 gr. gave 0.8032 gr. of carbonic dioxide and 0.1770 gr. of water.

II. 0.2946 gr. gave 0.7047 gr. of carbonic dioxide and 0.1520 gr. of water.

III. 0.2528 gr. gave 0.1200 gr. of magnesic pyrophosphate.

IV. 0.2492 gr. gave 0.1200 gr. of magnesic pyrophosphate.

V. 0.3424 gr. gave 40.44 c.c. of nitrogen at a temperature of 20°.5 and a pressure of 757.3 m m.

	I.	II.	III.	IV.	V.	Mean.
Carbon	65.34	65.24	—	—	—	65.29
Hydrogen	5.86	5.73	—	—	—	5.79
Phosphorus	—	—	13.25	13.47	—	13.36
Nitrogen	—	—	—	—	13.38	13.38

These results agree most nearly with the formula $(C_6H_5NH)_8P_4OH_2$, but are not far removed from $(C_6H\ NH)_7P_3O_2H_2$, as is shown by the following comparison: —

	Calculated for $(C_6H_6N)_8P_4OH_2$	Mean of analytical results.	Calculated for $(C_6H_6N)_7P_3O_2H_2$.
Carbon	65.61	65.29	65.37
Hydrogen	5.71	5.79	5.70
Phosphorus	14 12	13.36	12.06
Nitrogen	12.75	13.38	12.71

According to the first of these formulas the substance would be a derivative of the red oxide or hydrate of phosphorus, while the second can be developed into $[(C_6H_5NH)_3P]_2H_2O_2PC_6H_5NH$; it is possible, therefore, that a study of the decomposition-products of the substance might throw light on its composition. With this view we heated some of it to 140° in a sealed tube with hydrochloric acid, and obtained phosphorous and phosphoric acids, aniline chloride, some carbon, and an odor of phenol, but no red product; we have also found that boiling aniline with the red substance, so often mentioned, does not give this compound melting at 208°, so that our results are in favor of the second formula so far as they go, but need revision before much weight can be given to them.

Properties. The substance crystallizes in small white prisms apparently of the monoclinic system, or in long radiating needles with, as far as we could determine, the same melting-point and composition as the prisms; it melts at 208°, and is insoluble in water, freely soluble in hot alcohol, less so in cold, essentially insoluble in ether. Potassic hydrate in aqueous solution does not act on it at first, but gradually decomposes it if the two are boiled together; sulphuric acid acts in the same way; the decomposition with hydrochloric acid has been described already.

Substance Melting at 150°. This compound was obtained at the very end of the term in an attempt to prepare more of the substance melting at 208°; on this account we cannot give the conditions which determine its formation, or anything more concerning it than the following analyses: —

0.3492 gr. of substance gave 0.7122 gr. of carbonic dioxide and 0.2004 gr. of water.

0.2562 gr. gave, according to Carius, 0.1330 gr. of argentic chloride and 0.0890 gr. of magnesic pyrophosphate.

	Found.
Carbon	55.62
Hydrogen	6.37
Chlorine	12.83
Phosphorus	9.70

It would not be worth while to attempt to determine the formula of this substance until these results have been tested by further analyses. It crystallizes in rather thick white radiating needles, melts at 150°, and resembles the preceding substance in a general way in its solubility.

At no distant date we hope to be able to return to the study of

this subject in order to determine the nature of the two substances just described, to investigate more thoroughly the products of the reaction, which are soluble in water, and to take up the compounds formed by aniline and phosphorous trichloride in presence of diluents, which, according to a preliminary experiment, promise to be of great interest.